# PREPARATION, PROPERTIES AND DURABILITY STUDIES OF HDPE – KENAF CORE FILLER COMPOSITES

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# PREPARATION, PROPERTIES AND DURABILITY STUDIES OF HDPE – KENAF CORE FILLER COMPOSITES

**by**

**ASHRAF ROHANIZA BINTI ASARI**

**Thesis submitted in fulfillment of the requirements**

**for the degree of**

**Master of Science**

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## DECLARATION

I declare that the content presented in this dissertation is own my work which was done at Universiti Sains Malaysia unless onformed otherwise. This dissertation has not been previously submitted for any other degree.

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Date: 24 June 2013

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| ASTM | American Society of Testing and Materials |
| ATR | Attenuated total reflectance |
| DP | Degree of polymerization |
| DTG | Differential thermogram |
| DSC | Differential scanning calorimetry |
| EB | Elongation at break |
| FRIM | Forest Research Institute Malaysia |
| FSP | Fiber saturation point |
| FTIR | Fourier transform infrared spectroscopy |
| HALS | Hindered amine light stabilizer |
| HDPE | High density polyethylene |
| HMW-PE | High molecular weight polyethylene |
| KBr | Potassium bromide |
| KCF | Kenaf core fillers |
| LDPE | Low density polyethylene |
| LKTN | National kenaf tabacco board |
| LLDPE | Linear low density polyethylene |
| MFI | Melt flow index |
| MAPE | Maleated polyethylene or maleic anhydride polyethylene |
| MAPP | Maleated polypropylene or maleic anhydride polypropylene |
| OH | Hydroxyl group |
| PCL | Poly (caprolactone) |

| | |
|---|---|
| PBS | Poly (butylene succinate) |
| PE | Polyethylene |
| PEG | Poly (ethylene glycol) |
| PEMSB | Polyethylene malaysia sdn. Bhd |
| PLA | Poly (lactic acid) |
| PP | Polypropylene |
| SEM | Scanning electron microscopy |
| TGA | Thermogravimetric analysis |
| UHMW-PE | Ultrahigh molecular weight polyethylene |
| UV | Ultra violet |
| UVA | Ultra violet absorber |
| WF | Wood flour |
| WPCs | Wood plastic composites |
| XRD | X-ray diffraction |

## LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| °C | Degree celsius |
| ΔE | Total color change |
| $\Delta H_f$ | Heat of fusion |
| ΔL | Change in lightness |
| ρ | Density |
| 2θ | Diffraction angle |
| D | Diffusion coefficient |
| $I_c$ | Crystallinity index |
| M∞ % | Percentage of water uptake |
| rpm | Rotation per minute |
| Tg | Glass transition temperature |
| $X_c$ | Degree of crystallinity |

**PENYEDIAAN, SIFAT - SIFAT DAN KAJIAN KETAHANAN KOMPOSIT**

**HDPE – PENGISI TERAS KENAF**

## ABSTRAK

Komposit kayu plastik (WPCs) disediakan dengan menggunakan polietilena berketumpatan tinggi (HDPE) sebagai matrik, polietilena dicangkuk maleik anhidrat (MAPE) sebagai agen penserasi dan dua jenis pengisi digunakan iaitu pengisi teras kenaf (KCF) dan serbuk kayu (WF). Parameter- parameter yang dikaji untuk peringkat pertama adalah kesan penambahan MAPE, kesan bebanan pengisi dan kesan jenis pengisi terhadap sifat WPCs. Pengisi disebatikan dengan HDPE menggunakan mesin pencampur dalaman dengan peratusan berat pengisi adalah 0, 20, 40 dan 60% manakala MAPE ditambah sebanyak 5% berdasarkan berat kering pengisi. Penambahan MAPE kedalam WPCs meningkatkan kestabilan tork, ketumpatan, kekuatan tensil, modulus tensil dan terikan manakala indeks aliran leburan (MFI) dan darjah kehabluran ($X_c$) menurun. Peratus penyerapan air berkurangan sebanyak 29% untuk komposit terisi KCF manakala 33% untuk komposit terisi WF. Komposit terisi kenaf meningkatkan darjah kehabluran, kekuatan tensil, modulus tensil, kekuaan lenturan, modulus lenturan dan juga peratusan penyerapan air manakala indeks aliran cair, ketumpatan, kestabilan terma dan kekuatan hentaman adalah rendah jika dibandingkan dengan komposit terisi WF. Peringkat kedua adalah kesan pencuacaan terpecut terhadap WPCs. Sampel dicuacakan didalam kebuk pencuacaan xenon selama 500, 1000, 1500, 2000, dan 3000 jam. Dua kitaran pencuacaan digunakan iaitu pendedahan kepada cahaya xenon bersama semburan air dan pendedahan kepada cahaya xenon sahaja. Pendedahan kepada cahaya

UV dengan semburan air memberikan kesan yang teruk terhadap sifat mekanikal. Perubahan warna, sifat lenturan, indeks karbonil, indeks vinil, darjah kehabluran dan morfologi permukaan disukat selepas pencuacaan. . Untuk HDPE, kekuatan lenturan menurun tetapi modulus lenturan meningkat manakala kekuatan dan modulus lenturan untuk WPCs berkurang selepas 3000 jam dalam pendedahan terhadap cahaya UV dengan semburan air. $X_c$ WPCs meningkat pada peringkat awal tetapi semakin berkurang apabila masa pendedahan dipanjangkan. Perubahan kecerahan meningkat untuk WPCs yang didedahkan ke cahaya UV dengan semburan air mahupun terhadap cahaya UV sahaja. Indeks karbonil komposit lebih tinggi daripada HDPE dalam kedua – dua keadaan pencuacaan. Pendedahan sampel terhadap cahaya UV dengan semburan air memberikan indeks karbonil dan vinil yang lebih tinggi jika dibandingkan dengan pendedahan terhadap cahaya UV sahaja.

**PREPARATION, PROPERTIES AND DURABILITY STUDIES OF**

**HDPE – KENAF CORE FILLER COMPOSITES**

## ABSTRACT

Wood plastic composites (WPCs) were prepared using high density polyethylene (HDPE) as a matrix, maleic anhydride grafted polyethylene (MAPE) was used as coupling agent and two types of natural fillers were used which are kenaf core filler (KCF) and wood flour (WF). Parameters studied for the first stage are effect of incorporation MAPE, effect of different fillers loading and effect of different types of fillers on mechanical, thermal and water absorption properties of WPCs. Filler was compounded with HDPE by using internal mixer, filler weight fraction were 0, 20, 40 and 60%. WPCs incorporated with MAPE increased the stabilized torque, density, tensile strength, tensile modulus and strain while melt flow index (MFI) and degree of crystallinity ($X_c$) reduced. Percentage of water uptake reduced by 29% for KCF filled HDPE while 33% for WF filled HDPE composite if compared to uncoupled system. Density, tensile modulus, flexural strength, flexural modulus and percentage of water uptake also increased while $X_c$, MFI, strain and impact strength reduced for WF filled composite. KCF filled composite increase stabilized torque, $X_c$, tensile strength, tensile modulus, flexural strength, flexural modulus and percentage of water uptake if compared to WF filled composite. MFI, density, thermal stability, strain and impact strength are lower than WF filled HDPE composite. Second stage is effect of accelerated weathering on WPCs. HDPE and WPCs samples were weathered in xenon- arc weathering chamber for 500, 1000, 1500, 2000, 2500, and 3000 hours. Two weathering cycles were

employed which are exposure to xenon light with water spray and exposure to xenon light only. Exposed to UV light with water spray gave crucial effect on mechanical properties of WPCs and HDPE since water accelerate degradation process. Color change, flexural properties, carbonyl index, vinyl index, $X_c$ and surface morphology are measure after weathering For HDPE, flexural strength reduces but flexural modulus increased while flexural strength and modulus of WPCs reduce after 3000 hours when exposed to UV light with water spray. $X_c$ of WPCs were increased at initial stages but prolong exposure time reduced $X_c$ of WPCs. Changes in lightness increased for WPCs when exposed to UV light with water spray or to UV light alone. Carbonyl index of WPCs were higher than HDPE in any conditions but vinyl index of HDPE was the highest in both conditions. Carbonyl index and vinyl index of samples usually higher in exposure of UV light and water spray if compared to UV light alone.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Wood-plastic composites (WPCs) have received awareness in many applications due to the diverse advantages offered. WPCs solved environmental problems due to the use of biodegradable materials and reduced the usage of non-renewable resources. Natural fillers can obtained from waste products or agro based plant to get the fillers/fibers. Besides that, WPCs give special aesthetics properties of the composites which wood-like looking products (Mantia and Morreale, 2008). WPCs are widely used in automotive, household, and building applications. Built products are needed to expose WPCs in outdoor environment. Therefore, the effect of weathering on the visual appearance and chemical changes of WPCs are investigated (Li, 2000). Since the weathering test require long time periods, accelerated tests try to provide similar exposure in shorter time and introduces the factor of continued irradiation (Richardson and Lokensgard, 1997; Philip et al, 2004). Exposed samples are rated on color change, chemical changes, and loss of physical properties (Stark and Matuana, 2004a). There are many factors can lead to weathering of WPCs such as solar radiation, temperature, humidity, oxygen and more (Stark and Gardner, 2008; Rowell et al, 1997b; Chaochanchaikul *et al*, 2012). In this study, effect of solar radiation and water spray is investigated.

The mechanical properties of WPCs reduce when exposed to water. The hydrophilic nature of natural fillers is responsible for the water absorption in natural fillers/ thermoplastic composite. Natural fillers/ fibers contain various hydroxyl groups that are

strongly hydrophilic (Stark, 2007; Chaochanchaikul et al, 2012). The rate at which water is absorbed by a composite depends on many variables including filler/fiber type, matrix, temperature, the difference in fillers distribution within the composite, and reaction between water and the matrix (Najafi et al, 2008). Photodegradation of polyolefins originates from excited polymer–oxygen complexes and is caused mainly by the introduction of chromophore groups such as catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds introduced during polymer manufacturing (Stark, 2007). The presence of lignin, cellulose, hemicellulose, and extractives in natural fillers are variously susceptible to photodegradation. The weathering is confined to the surface and involves photo-induced breakdown of lignin to water-soluble reaction products. Lignin is the major component degrades during photo – oxidation process (Rowell, 2005).

### 1.2 Problem statement

The awareness in producing eco-friendly product has been widely studied together with the rising of environmental consciousness worldwide. Examples of eco-friendly products in polymeric industries are producing biodegradable thermoplastic such as poly (lactic acid) (PLA), poly (caprolactone) (PCL), poly (butylene succinate) (PBS), poly (ethylene glycol) (PEG) and more (Tserki et al, 2006). Besides that, there are combination of natural fillers/fibers and thermoplastic either the virgin or recycled to produce composite. In this study, the focus on the incorporation of natural filler from waste products which is wood flour and kenaf core filler which come from agro based fiber crops. Virgin high density polyethylene (HDPE) is use as a matrix. Natural fillers are renewable and biodegradable materials and have the potential to act as reinforcing

filler in composite (Kim et al, 2007). With incorporation of natural fillers into existing thermoplastic, it will replacing the portions of petroleum – based thermoplastic and produced composite materials.

Combination of natural fillers/fibers and thermoplastic have problem in compatibility and hence give low interfacial adhesion between fillers and matrix. This low compatibility gives crucial effect in mechanical properties and the end use of the wood plastic composites (WPCs) (Kim et al, 2007). To increase the compatibility of these two constituents, there are various treatments can be use either surface modification of natural fillers/fibers, used of coupling agents or plasma irradiation (Kim et al, 2006). Hydrophilic nature of natural fillers/fibers makes them very sensitive to water. Natural fillers/fibers tend to absorb water molecules and cell wall of their structure will swell. In case of WPCs, the swelled cell wall will create microcracks in the thermoplastics and produce gaps between filler matrix interfacial region (Stark, 2007; Chaochanchaikul et al, 2012). As the process is continuous, the mechanical properties of WPCs will decrease. Therefore effect of weathering was studied since both wood and matrix involving in photo-oxidation process (Stark, 2007).

## 1.3 Research objectives

1. To investigate the effect of addition maleic anhydride grafted polyethylene (MAPE) towards the mechanical properties of composites.

2. To investigate effect of fillers loading towards the mechanical properties of HDPE and kenaf core fillers with composite of HDPE and wood flour.

3. To compare the mechanical properties and water absorption behavior of composites from different type of fillers.

4. To determine the effect accelerated weathering periods and weathering factors on the appearance, chemical and mechanical properties of the composite.

## 1.4 Scope of research

In this research, usage of kenaf core filler (KCF) was highlight as the substituent fillers in composite industry. There are several reasons in using KCF as filler which are high percentage of core part than bast part in kenaf stem. Besides that, Kenaf trees are commercialized plant as agro based fiber crops while wood flour was obtained from post consumer product. Kenaf also known as fast growing plant which can reduce problem of depletion source in fillers.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Wood plastic composites (WPCs)

Composite is defined as a combination of two or more materials with new properties obtained if compare to single material (Rosato and Rosato, 2005). Composites also can occur by naturally. Example of natural composite is sedimentary rocks which the particles are held together by natural cement. Wood is also a natural composite due to cellulose fibers were held together with a matrix of lignin (Rosato and Rosato, 2005). Wood plastic composites (WPCs) are defined as the composites that contain wood (in any form) and thermoplastic as well as thermoset (Clemons and Caufiled, 2005). In WPCs, term natural fillers and fibers being used since both of them consist same chemical compositions. However there are some differences between these two terms. Natural fibers are referring to individual fibers which have a potential to improved mechanical properties such as strength, elongation and un-notched Izod impact energy. Therefore, natural fibers have been chose as reinforcement in WPCs. Natural fillers are referring to wood in particulate form or very short fibers. Natural fillers are relatively in high bulk density and free flowing nature if compare to natural fibers which means natural fillers easier to be process especially in feeding section. (Rowell, 2005). Development of WPCs growth since the awareness in producing green environment products becomes crucial. Adding natural fillers in thermoplastic will reduce the percentage of thermoplastic and hence reduce the consumption of non – biodegradable materials (Li, 2000; Tserki et al, 2006). There are many advantages of developing WPCs

such as to use smaller trees, to use waste from other processing, to remove defects, to create more uniform components, to develop composites stronger than original solid wood and to be able make composites of different shapes (Rowell, 2005).

Combining natural fillers and plastics also reduce material cost if compared to synthetic fibers for instance carbon and glass fibers, produce composite materials that give synergistic effect than individual components and have lower weights (Abu Sharkh and Hamid, 2004; Rowell et al, 1997; Jonoobi et al, 2009). Filler content in matrix was depends on the end use of WPCs since higher filler loading can reduce thermal stability of composites. Therefore, it is important to consider the fiber orientation, fiber loading, compatibility between matrix and fiber to ensure sufficient stress transfer from matrix to fiber. WPCs are widely used either in non – structural or semi- structural applications such as roofing tiles, deck and floor. (Stark and Matuana, 2004a). Applications of WPCs are more toward building applications, therefore durability of WPCs against weathering, particularly ultraviolet (UV) and water (Kiguchi et al. 2007; Muasher and Sain. 2006; Stark and Matuana, 2004a) were studied. Other disadvantage of natural fibers/thermoplastic composites is low compatibility between hydrophobic matrix and hydrophilic fibers. Low compatibility contributed to the formation of low interface which lead to low mechanical properties. To improve compatibility of fibers and matrix, coupling agent can be used or conduct chemical treatment towards the fibers (Sanadi et al, 1997).

(a) (b)

Figure 2.1: Application of wood plastic composites: (a) extruded wood fiber plastics, and (b) roofing tiles (Rowell, 2005)

## 2.2 Matrix Phases

Matrix may be a metal, ceramic or polymer. In case of this study, polymer is use as a matrix. There are several functions of matrix in WPCs. First, matrix binds all fillers/fibers together and acts as a medium to stress transfer to fillers/fibers (Callister, 2003). Besides that, matrix also protects fillers/fibers from being damage during mechanical processing or chemical interactions (Callister, 2003). Thermoplastics are the high demanding material in various applications since it readily molded into complex shapes that are mostly high cost if use material from metals or ceramics. The applications are wide including in packaging industry, household goods, industrial components, automotive parts and more (Juran, 1990). Thermoplastic was a good choice since it can be repeatedly heated, fabricated and cooled. Therefore, their scraps were recyclable. Examples of thermoplastics are acrylic, nylon, polystyrene, polypropylene and polyethylene. Thermoplastics have superior toughness if compared to thermosets. Their structures are mostly linear although the chains may be branched, which not form

a rigid network like thermosets (Matthews and Rawlings, 1994). Bonding between the chains is due to Van der Waals force which is weak and can be easily break due to thermal activation and applied stress (Matthews and Rawlings, 1994). Tensile strength and tensile modulus of thermoplastic was not high as thermosets. Therefore, thermoplastic usually added with reinforcement fillers to enhance mechanical properties together with reduce percentage of virgin plastics. Table 2.1 shows some properties of thermoplastics.

Table 2.1: Properties of some thermoplastics (Matthews and Rawlings, 1994).

| **Properties** | **Acrylic (PMMA)** | **Nylon (6.6)** | **Polycarbonate** | **Polypropylene** |
|---|---|---|---|---|
| Density ($g/cm^3$) | 1.2 | 1.1 | 1.1-1.2 | 0.9 |
| Young's modulus (GPa) | 3.0 | 1.4-2.8 | 2.2-2.4 | 1.4-1.9 |
| Tensile strength (MPa) | | 60-70 | 45-70 | 25-38 |
| Ductility (%) | | 30-100 | 90-110 | 100-600 |
| Glass transition temperature (°C) | 90-105 | | 150 | |
| Melting temperature(°C) | | 261 | | 175 |

2.2.1High density polyethylene (HDPE)

Polyethylene (PE) backbone consists of two carbons and four hydrogens as its repeating unit (Strong, 2006). Polymer units of PE are shown in Figure 2.2. There are various sub group of thermoplastics arise from PE such as low density polyethylene (LDPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), high molecular weight polyethylene (HMW-PE) and ultrahigh molecular weight

polyethylene (UHMW-PE). All of mentioned polymers are distinguished on the basis of density (Matthews and Rawlings, 1994). Besides that, the differences of each polymer depend on polymerization condition. For example LDPE were polymerized under high temperature and high pressure. The density of this polymer is low since it conditions resulted in formation of many long branches which are difficult to pack close together (Strong, 2006). Another example of PE was LLDPE which is polymerized under low temperature and low- pressure catalyst process which produced longer and branches chains (Strong, 2006). Therefore it has low density as LDPE but linear structure as HDPE.

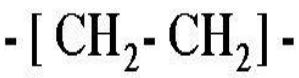

Figure 2.2: Polyethylene structure

HDPE is one of the top volumes of thermoplastic in the world (Rowell, 2005). HDPE is polymerized under low pressure and temperature together with Ziegler-Natta catalyst which give linear chains with limited and short branches (Strong, 2006). HDPE is highly crystalline, non polar thermoplastic. Due to it's linear structure, it able to attain up to 90% of crystallization (Richardson and Lokensgard, 1997). Polymer chains of HDPE are easily packed tightly to form crystalline structure hence increase the density. Increase in density gave high stiffness, softening point, tensile strength, crystallinity and creep resistance but will reduces impact strength, elongation, flexibility as well as transparency (Richardson and Lokensgard, 1997). HDPE usage covers many fields including milk, water and detergent bottles since it give sufficient stiffness. Besides that, it also well use as barrels, trash cart, automotive fuel tanks due to it superb chemical

resistance, low permeability and sufficient strength given. Since HDPE is less optically clear than LDPE, therefore, HDPE is mostly use in unimportant visual clarity applications (Strong, 2006).

(a) (b)

Figure 2.3: Schematic of (a) linear arrangement of HDPE and (b) branched arrangement of LDPE.

Other properties of HDPE such as excellent chemical resistance, and does not absorb moisture which suitable for packaging applications. Besides that, it also has good electrical properties which suitable for cable applications (Juran, 1990, Richardson and Lokensgard, 1997). There are various fabrication process can be choose such as injection molding, sheet extrusion, pipe or profile extrusion, blow molding and rotational molding (Juran, 1990).

Table 2.2: General properties of HDPE (Richardson and Lokensgard. 1997).

| | |
|---|---|
| Density ($g/cm^3$) | 0.941-0.965 |
| Tensile strength (MPa) | 20-38 |
| Impact strength, Izod (J/mm) | 0.025-1.0 |
| Water absorption, 24hours (%) | 0.01 |
| Effect of sunlight | Crazes – must be stabilized |

## 2.3 Natural fillers

As the availability of solid wood decreased, wood industry looked the alternatives to produce smaller diameter trees and saw pulp mill wastes (Rowell, 2005). Besides that, the development of agro- based fiber field also gave positive effect on solving depletion of natural filler in composites and paper industry (Rowell et al, 1997b). Figure 2.4 shows the breakdown of solid wood which can be used to produces composites materials. Besides that, non-wood material is also another type of celluloses which is intentionally plants to get the fibers or fillers (Jonoobi et al, 2009). Fillers are used in large quantities to provide an improvement in some properties such as strength, stiffness, reduce percentage of matrix, and reduce cost (Rosato and Rosato, 2005; Clemons and Caufiled, 2005; Jonoobi et al, 2009). Besides that natural fillers modify mechanical performance of thermoplastic without increase their density excessively (Clemons and Caufiled, 2005). Filler can be agricultural crop wastes such as wheat straw, bagasse, kenaf, corn also some forest waste products such as wood fibers, sawdust or chips and other recycled products (Rosato and Rosato, 2005). Suppliers of natural filler were diverged which can come from forest products companies such as lumber mills, furniture, millwork and window or door manufactures that produces natural fillers as by product. Moreover, there are also companies which are specializing in natural fillers/ fiber production (Rowell, 2005). There are many types of natural fillers/fibers available and the chosen fillers/fibers depend on slight color differences, regional availability, and familiarity (Clemons and Caufiled, 2005). As an example, red oak was used due to low molecular weight of phenolic compounds which can cause stains if the composites is repeatedly wetted (Clemons and Caufiled, 2005).

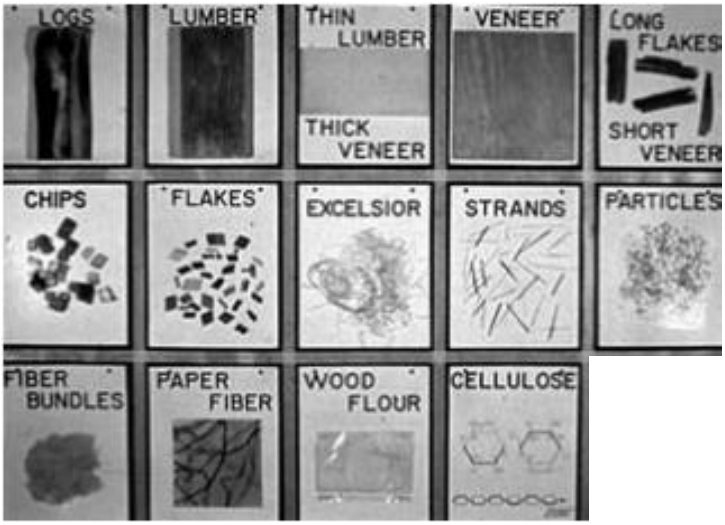


Figure 2.4: Basic wood elements, from largest to smallest (Rowell, 2005)

2.3.1 Composition and structure of natural fillers/fibers.

Natural fillers/fibers are a complex, three – dimensional, polymer composite made up primarily of cellulose, hemicelluloses and lignin. Each component responsible to particular properties as shown in Table 2.3. The relationship of strength and chemical composition is depend on polymeric component that make up the cell wall (Rowell, 2005).

Table 2.3: Cell wall polymers responsible for the properties of wood (Rowell, 2005).

| **Properties of natural fillers/fibers** | | **Chemical constituents** |
|---|---|---|
| **Moisture absorption** | I. | Hemicelluloses |
| | II. | Accessible celluloses |
| | III. | Non – crystalline celluloses |
| | IV. | Lignin |
| | V. | Crystalline cellulose |
| **Ultraviolet degradation** | I. | Lignin |
| | II. | Hemicelluloses |
| | III. | Accessible cellulose |
| | IV. | Non- crystalline cellulose |
| | V. | Crystalline cellulose |

| | | |
|---|---|---|
| **Thermal degradation** | I. | Hemicelluloses |
| | II. | Celluloses |
| | III. | Lignin |
| **Strength** | I. | Crystalline celluloses |
| | II. | Matrix (non – crystalline celluloses + hemicelluloses + lignin) |
| | III. | Lignin |
| **Biological degradation** | I. | Hemicelluloses |
| | II. | Accessible celluloses |
| | III. | Non- crystalline celluloses |
| | IV. | Crystalline cellulose |
| | V. | lignin |

Cellulose is made up by linear polymer of anhydroglucose units with both crystalline and amorphous regions. The cellulose chain may be 5000-10000 units long (Rowell, 2005). Cellulose is the main component providing the wood strength and structural stability. It was typically 60-90% crystalline by weight (Clemons and Caufiled, 2005). Hydrogen bond is believed to provide rigidity to the cellulose molecules via stress transfer and allow the molecules to absorb shock by subsequently breaking and reforming (Rowell, 2005). According to Aji et al (2009), anhydroglucose units contains three hydroxyl (OH) groups which form hydrogen bonds inside the macromolecules itself (intramolecular) and also with other cellulose molecules (intermolecular). This is the reasons of their hydrophilic properties.

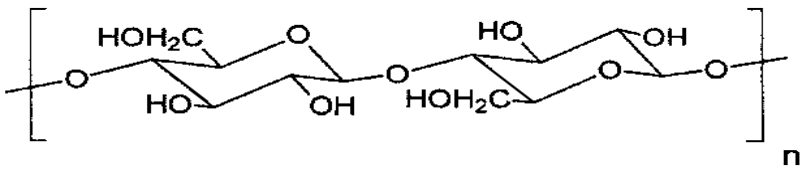


Figure 2.5: Chemical structure of cellulose (Rowell, 2005).

Hemicelluloses are branched polymers of polysaccharide with average degree of polymerization (DP) is 100-200 which is well below of cellulose (Jonoobi et al, 2009; Clemons and Caufiled, 2005; Rowell, 2005). Hemicellulose contains mainly the sugars D-xylopranose, D-gluvopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amounts of other sugars (Rowell et al, 1997b; Rowell, 2005). Hemicelluloses usually consist of more than one type of sugar unit and are sometimes referred to the sugar they contain such as galactoglucomannan, arabinoglucuronoxylan, arabinogalactan, glucoronoxylan, glucomannan and more. Hemicelluloses also contain acetyl and methyl substituted groups (Rowell et al, 1997b; Rowell, 2005). Hemicelluloses are hydrophilic and dissolve in alkaline and easy to hydrolyze by acids (Mohanty et al, 2005). Detailed structure of wood hemicelluloses has not been determined. Only the ratios of sugars that these polysaccharides contain have been studied.

Lignins are amorphous, highly complex, mainly aromatic, polymers of phenylpropane units. All plants lignins consist mainly of three basic building blocks of guaiacyl, syringyl and p- hydroxyphenyl groups. There is wide variation of structures within different plants species. The phenylpropane can be substituted at the α, β and γ positions into various combinations linked together both by ether and carbon to carbon linkage (Rowell et al, 1997b; Rowell, 2005) as shown in Figure 2.6. Lignin is a component which acts as a binder in plant. It is a copolymer which contains aliphatic and three dimension, complex aromatic groups with high molecular weight. Lignin is characterized as a component which had high carbon content but low hydrogen content. Lignin is amorphous and hydrophobic (Mohanty *et al*, 2005).

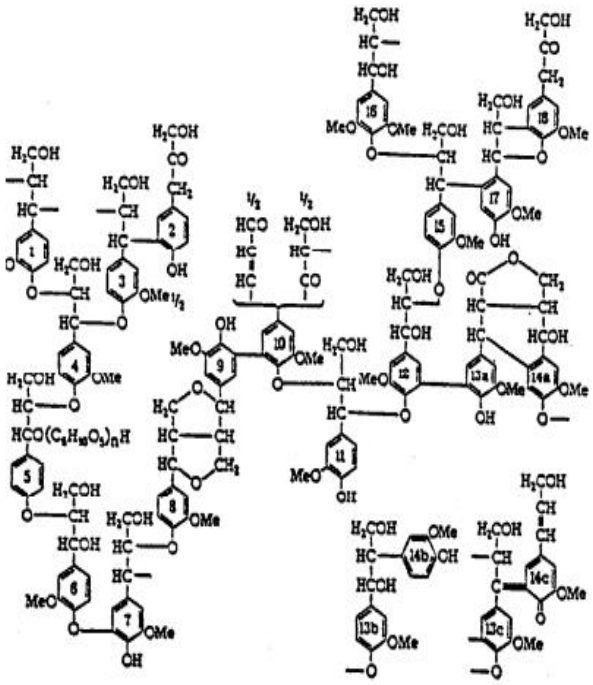

Figure 2.6: Partial structure of lignin (Rowell *et al,* 1997b).

2.3.2 Advantages of natural fillers / fibers

Natural fillers/fibers present many advantages if compared to inorganic fillers such as low density and cost. Besides that, it also less abrasive to processing equipment, from renewable resources, biodegradable, low energy consumption, easy surface treatment, and their mechanical properties can be comparable with composite filled with inorganic fiber (Aji et al, 2009; Rowell et al, 1997). According to Rowell et al (1997), specific tensile and flexural modulus of 50% by weight of kenaf filled polypropylene (PP) composite were comparable with 40% by weight of glass fiber filled PP injection molded composite. High filling level also possible by using natural filler and hence reduced the consumption of thermoplastic. Wood-like appeal is one of the advantages of natural fillers. Using solid wood will drag to excessive cost and depletion of natural resources, therefore, add natural filler to plastic can impart similar aesthetical appeal

properties as using solid wood (Clemons and Caufiled, 2005). Natural fillers/fibers are renewable materials and they are many different types of natural fillers/fibers available as shown in Table 2.4.

Table 2.4: Inventory of major potential world fiber sources (Sanadi et al, 1997).

| **Fiber sources** | **World (dry metric per tons)** |
|---|---|
| Wood | 1,750,000,000 |
| Straw (wheat, rice, oat, barley, rye, flax, grass) | 1,145,000,000 |
| Stalks (corn, sorghum, cotton) | 970,000,000 |
| Sugar cane bagasse | 75,000,000 |
| Reeds | 30,000,000 |
| Bamboo | 30,000,000 |
| Cotton staple | 15,000,000 |
| Core (jute, kenaf, hemp) | 8,000,000 |
| Papyrus | 5,000,000 |
| Bast (jute, kenaf, hemp) | 2,900,000 |
| Cotton linters | 1,000,000 |
| Esparto grass | 500,000 |
| Leaf (sisal, abaca, henequen) | 480,000 |
| Sabai grass | 200,000 |
| TOTAL | 4,033,080,000 |

### 2.3.3 Disadvantages of natural fillers / fibers

Primary disadvantage of using natural fillers/fibers is low thermal stability. Natural fillers tend to degrade at low temperature. Therefore, the processing temperature is limit to 200°C. Because of this reason, only several type of thermoplastics which have low melting temperature (below 200°C) can be use such as polyethylene, polypropylene, polystyrene and polyvinyl chloride (Rowell et al, 1997). Another disadvantage of using natural fillers/fibers is high moisture absorption. Natural filler is a hydrophilic material and tend to absorb water by hydrogen bonding. Water uptake by natural fillers/fiber will swell the fillers/fibers cell wall and form microcracks. Besides that, the dimension

stability of composite was change and it cannot be ignored (Rowell et al, 1997a; Rowell et al, 1997b). Water molecules act as external plasticizer on fillers/fibers properties by lowering the glass transition temperature (Tg). This will results in reduction of strength and stiffness of fillers/fibers (Rowell et al, 1997b). Therefore, many study were performed to reduced the absorption of water by chemical modification such as acetylation and propionylation treatment or by using coupling agent such as maleic anhydride polypropylene(MAPP) or maleic anhydride polyethylene (MAPE) (Tserki et al, 2006). Natural fillers/fibers also sensitive to UV light which gave severe effect to the performance of WPCs in outdoor applications (Ndiaye et al, 2008). Wood components such as cellulose, hemicelluloses and lignin were susceptible to undergo photodegradation (Stark, 2007). UV light will breakdown lignin components to water-soluble product which leads to the formation of choromphoric groups which tend to undergo further degradation (Stark, 2007). Therefore, several type of UV stabilizers usually use in producing a good UV resistance products such as pigment, Hindered Amine Light Stabilizer (HALS) and Ultra Violet Absorber (UVA).

### 2.3.4 Kenaf core filler (KCF)

Kenaf (Hibiscus Cannabinus L.) is herbaceous plant that can be grown under wide range of weather conditions and kenaf can grow to more than 3 meters within 3 month (Aji et al, 2009). Optimum temperature for kenaf growth is between 22 and 30°C, annual moisture requirement is low which 150 mm in a soil pH between 6.0 and 6.8. Kenaf has a growing cycle of 150 to 180 days with an average yield of 1700 kg/ha (Rowell and Stout, 2007). Jonoobi et al (2009) state that kenaf is one of non-wood lignocelluloses that have a great potential for industrial applications. In United States,

kenaf is harvested by using modified sugarcane equipment or forage chopping equipment.

However, kenaf is sensitive to frost. Hot and humid climates in Malaysia make it suitable for kenaf plantation. The existing of National Kenaf Tabacco Board (LKTN) proves Malaysian government support the development of kenaf due to kenaf can increase the state income since competition on tobacco was high due to other largest producer of tobacco (Alias, 2007; Jonnobi et al, 2009). It is cultivate from seed for the bast and core fibers are produce in the stem. Long bast fibers are produced in the outer bark while the shorter core fibers are produced in the interior portion of the stem (Rowell et al, 1997b). High interest in kenaf cultivation has been achieved due to its ability to absorb nitrogen and phosphorus included in soil. Besides that kenaf also can accumulate carbon dioxide at high rate which can prevent global warming problem (Aji et al, 2009).

There are various applications of kenaf can be obtained such as oil-spill adsorbents, livestock bedding, packing materials, filters, textiles, fiberboard, and also non-woven mats in the automotive industries (Rowell et al, 1997b; Aji et al, 2009). Due to avoiding destruction of forests, kenaf also is selected as an alternative of wood in pulp and paper industries. There is new development in automotive industries involving kenaf fibers. In 2000, Toyota Boshoku group invented door trim base of kenaf fiber and PP resins. Besides that, they also produce spare tyre covers using kenaf and Polylactic acid (PLA) which is 100% biodegradable.

2.3.5 Wood flour (WF)

There is various type of wood flour available and it depends on the species of the tree. Examples of WF are made of oak, pine, maple and more. The main step in producing WF is size reduction. Large solid wood will be reducing in size by using hammer mill, hog or chipper. The coarse wood will pulverize by grinding or beating with impactors or crushing between rollers (Clemons and Caufiled, 2005). After pulverized, wood flour can be classified using vibrating, rotating or oscillating. Wood flour size usually referred by standard mesh size and their particle diameters. High cost is subject to the fine wood flour as well as increasing the melt viscosity (Clemons and Caufiled, 2005). WF in this study is Meranti which is a common name applied to four groups of Shorea from Southeast Asia especially Malaysia, Indonesia and Philippines (Miller, 1999). There are four groups of meranti which differentiate based on their heart wood color and weight as shown in Table 2.5.

Table 2.5: Classification of Meranti groups (Miller, 1999).

| **Name** | **Color** | **Density of air-dried wood** |
|---|---|---|
| Dark red meranti (also called tanguile and dark red seraya) | Dark brown; medium to deep red, sometimes with a purplish tinge | 640+ $kg/m^3$ |
| Light red meranti (also called red seraya) | Variable—from almost white to pale pink, dark red, pale brown, or deep brown | 400 to 640 $kg/m^3$, averaging 512 $kg/m^3$ |
| White meranti (also called melapi) | Whitish when freshly cut, becoming light yellow-brown on exposure to air | 80 to 870 $kg/m^3$ |
| Yellow meranti (also called yellow seraya) | Light yellow or yellow-brown, sometimes with a greenish tinge; darkens on exposure to air | 480 to 640 $kg/m^3$ |

Meranti species have coarse texture, do not have dark colored deposits in pores, and had interlocked grain. They have axial resin ducts aligned in long, continues, and tangential lines as seen on the end surface of the wood. In term of processing characteristics, all meranti groups are easily to machine except white meranti which result in dulls cutters due to high silica content (Miller, 1999). The light red and white meranti are easily to dry without degradation while dark red and yellow meranti dry more slowly and tend to wrap. The light red, yellow and white meranti do not durable in exposed condition or in ground contact not like dark red meranti. There are many uses of meranti products such as hardwood plywood, joinery, furniture and cabinetwork, moulding and millwork, flooring and general construction (Miller, 1999).

**2.4 Coupling agent**

Coupling agent is a chemical which use to improve the adhesion between two phases in a composites material (Pritchard, 1998). Two phases here refer to polymer matrix and natural fillers. These two materials have different polarities which lead to poor interfacial bonding between them. According to Callister (2003), better interaction between fillers and matrix need to achieve to provide better stress transfer from matrix to fillers which hence increase the strength of composites and minimize the filler pull-out. Therefore, many researchers suggest the usage of coupling agent in enhance the mechanical properties as well as low cost if compared to other chemical surface treatment. Maleic anhydride grafted polyolefin is well known coupling agent which consist different polar groups.

There are two different mechanisms of MAPE reactions. Firstly, maleic anhydride groups were form ester bond with hydroxyl groups from natural fillers/fibers.

It is important to be note that maleic anhydride groups also tend to form hydrogen bonding with hydroxyl groups of natural fillers/fibers (Rowell et al, 1997b). Interaction of PE segment in MAPE and PE are chain entanglements (Rowell, 2005; Rowell et al, 1997b). These entanglements function are similar to physical crosslink which give mechanical integrity to the composite. Polymer chains in coupling agent should be long enough to permit entanglement with matrix in the interphase (Rowell et al, 1997b). If the polymer chains are short, the chance of PE from MAPE and PE from matrix to entangle is low and they are easily to slide past one another. However if the chains are extremely long, MAPE will entangle with the matrix, but the polar groups on the MAPE will have difficulty in finding OH group in fiber surface (Rowell et al, 1997b).

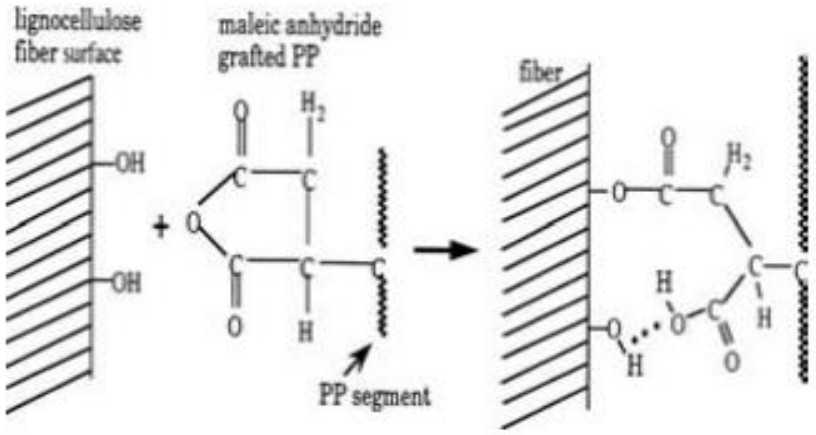


Figure 2.7: Reaction mechanism of MAPP with natural fillers surface (Rowell et al, 1997b)

## 2.5 Water absorption

Hydroxyl groups and other oxygen-containing groups in natural fillers/fibers are responsible in attract water molecules through hydrogen bonding. As state in Table 2.3, hemicelluloses is the major component in moisture absorption, but the accessible cellulose, non-crystalline cellulose, lignin and surface of crystalline cellulose also play a major role in water absorption properties (Rowell et al, 1997b). Since WPCs are mostly in outdoor purpose, it is needed to evaluate the water uptake characteristic since it influence the final application and span life of WPCs (Tajvidi et al, 2005). There are many variables effect the rate of water absorption such as interfacial bonding between matrix and fillers, fillers/fibers type, matrix, temperature and the difference in water distribution within the composite (Najafi et al, 2008). Water absorption will affect the dimension of WPCs, span life of WPCs and mechanical properties such as strength and modulus (Stark and Gardner, 2008). Figure 2.8 shows an illustration of water absorption mechanism.

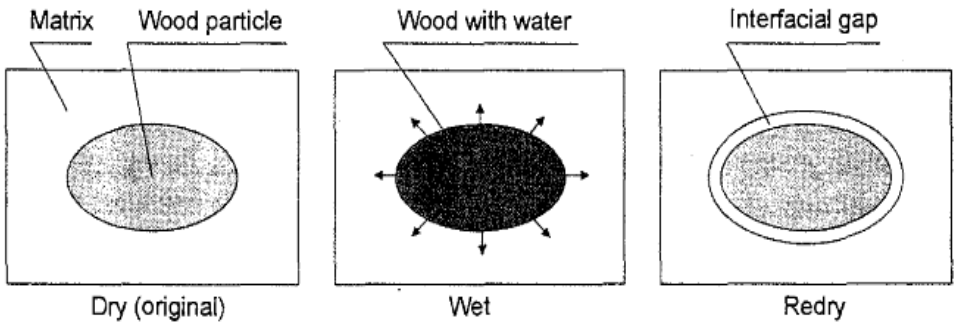


Figure 2.8: Schematic of moisture damage in WPCs (Stark and Gardner, 2008).

Adhesion between filler and matrix of WPCs is shown in dry condition. When there is water molecules in contact, filler will absorb water molecules through hydrogen bonding and cause filler to swell. This phenomenon will creates stress in both fillers

matrix and which lead to the formation of microcracks. Besides that, fillers also experience stress (Stark and Gardner, 2008). As WPCs is still in water contact, water molecules keep being absorbed until filler cell wall saturated with water. When filler cell wall already saturated, it is known as fiber saturation point (FSP) and beyond this point, water molecules act as free water which means no further expansion can occur (Rowell et al, 1997b). After drying the WPCs, the filler will shrink as it loses water molecules below it FSP and left interfacial gap between filler and matrix. Since there are cracks and interfacial gaps produced during exposing water to WPCs, it will provide sites for further penetration of water and other degradation variables.

### 2.6 Accelerated weathering

Weathering is surface degradation of wood that is initiated primarily by ultraviolet (UV) portion of solar spectrum but other factors also contribute to the weathering (Rowell et al, 1997b). It is known as photo-oxidation or photochemical degradation of the surface (Rowell et al, 1997b). Accelerated weathering is a technique used to compare performance by subjecting the samples to cycle that are repeatable and reproducible since natural weathering take long time to perform (Stark and Gardner, 2008). During accelerated weathering, test standards such as radiation (ultraviolet, xenon arc, etc) and water spray (number and time of cycles) are followed. The behavior of WPCs during and after weathering are quite complex and depends on weathering variables such as radiation, moisture, wind, temperature, oxygen concentration, chemicals and more (Stark and Gardner, 2008; Rowell et al, 1997b; Chaochanchaikul et al, 2012). Accelerated weathering may end up with the changes in color of WPCs which affect aesthetic appeal and reduce mechanical properties of WPCs. Changes in

mechanical properties are due to composites surface oxidation, matrix crystallinity changes as well as interfacial degradation. Besides that, the combination of radiation and moisture gave crucial damaging effect on WPCs (Stark and Gardner, 2008; Chaochanchaikul et al, 2012). Weathering process affects only the surface of sample and it was a slow process.

Photo - degradation will affect both natural fillers and matrix and they act synergistic. During weathering, chemical constituent in wood component play important role in initiate the photo-oxidation process. Lignin is believed to be a main component photo-oxidation process. Exposing WPCs to UV radiation will degrades the hydrophobic lignin and water washed away the degraded lignin product and makes surface of WPCs contain hydrophilic celluloses groups. As the name implies on hydrophilic celluloses, it tends to absorb water molecules and increasing the surface wettability (Stark and Gardner, 2008). Besides that, swelling wood fiber will produce microcracks at the matrix- filler interphase and hence facilitate the penetration of light into WPCs (Stark and Gardner, 2008). As this process is keep going, the mechanical properties of WPCs will affect.

For photo-oxidation of polyolefin, the reaction also initially cause by the UV from solar radiation. Portion of UV light is between 290-400 nm, while an energy is between 412-300 kJ/mol. Basically, saturated hydrocarbon such as polyolefin does not absorb light above 250 nm but there are several reasons of this behavior. During processing and manufacturing of polyolefin, the polymer chains undergo changes in their structure such as cross-linking, chain scission and formation of double bonds (Stark and Gardner, 2008). Besides that, left residual catalyst, additives and pigment also exist